National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama

Contract No. NAS8-50

Quarterly Report No. 3
1 April 1961 to 30 June 1961

DEVELOPMENT OF CERAMIC FIBERS FOR REINFORCEMENT IN COMPOSITE MATERIALS

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15 July 1961

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I. SUMMARY

The efficiency of vertical arc fiberizing was improved by attaching a blast concentrator to the annular ring nozzle. The concentrator eliminated material blowback, almost doubled the fiber yield, and reduced the quantity of pellets formed.

The evaluation of a 20 degree annular ring nozzle indicated no improvement in fiber yield over the 30 degree nozzle.

Studies were conducted with a drip fiberizing method which consisted of blasting falling drops of material melted in the arc. The method showed considerable promise for continuous fiberizing of materials which require a short cooling delay time (i. e., rapid freezing).

Studies of a horseshoe shaped nozzle, also designed to reduce the cooling delay time, revealed that it considerably improved the operating ease of the vertical fiberizing apparatus and reduced the delay time to 0. 1 to 0. 2 second.

Of 35 new fiber compositions evaluated, eight materials showed promise in having acceptable fiber yields and fusion temperatures. Three materials had fusion temperatures exceeding 1800°C.

A brief study has demonstrated the feasibility of felting bulk fibers to eliminate pellets and to orient fibers preferentially in one plane prior to resin impregnation.

II. PURPOSE

The purpose of Contract No. NAS8-50 is to conduct research directed toward the development of ceramic fibers and ceramic fiber composites for use in space technology. The work shall include but not be limited to the following:

1. Develop refractory glass compositions with characteristics suitable for fiber forming.

2. Develop methods for forming fibers from the above refractory glass compositions.

3. Study the pertinent fiber forming parameters for each promising composition as necessary to achieve reproducibility.

4. Conduct physical, mechanical, and thermal property tests and petrographic analysis on promising fibers.

5. Fabricate fiber-matrix composite test specimens and conduct physical, mechanical, and thermal property tests on these specimens.

6. Furnish specimens to MSFC of promising fibers and composites (organic or inorganic matrix as required) obtained as a result of the above.

7. Develop quantity production methods for fiber forming.

8. Develop inorganic matrix materials compatible with the ceramic fibers; prepare test specimens and conduct property tests on these specimens.

9. Ascertain the feasibility of ceramic fiber-composite materials for use in structures for cryogenic and hyperthermal applications.

III. EXPERIMENTAL WORK

A. Arc Fiberizing

Improvement of Fiberizing Efficiency

Studies of two annular nozzle modifications were conducted in an effort to improve fiberizing efficiency.

Material blowblack around the rod through the top of the nozzle has been a relatively serious problem in causing fibers and pellets to jam the arc mechanism. To reduce this, two types of blast concentrators were fabricated. These concentrators consisted of one- and two-inch long funnels surrounding the blast cone and fastened to the underside of the nozzle. Both concentrators were very effective in completely eliminating blowback as well as producing acceptable quality fibers. The two-inch concentrator nearly doubled the previous fiber yield of R-74, produced more uniform fibers, and reduced the quantity of pellets. For these reasons this concentrator has been established as a standard annular nozzle attachment for all future fiberizing studies.

The second annular nozzle modification consisted of changing the blast impingement angle of the 45 degree nozzle to 20 degrees. Since a previous comparison of impingement angles of 30 and 45 degrees indicated a higher fiber yield with the 30 degree angle (Quarterly Report No. 2), it was felt that a yet smaller angle might also improve the yield. The results indicated a much lower yield with the 20 degree nozzle, only two grams per fifty blasts. The fibers were very coarse, but were uniform in diameter and texture. They were the longest fibers yet produced. One fiber was 6-1/2 feet long - the length of the fiber collecting chamber. However, because of the low yield, further work with this nozzle was not considered feasible at this time.

Reduction of Blast Delay Time

It has been ascertained that some of the high-melting fiber compositions require a short blast delay time from the

melt (i.e., rapid freezing) to produce fibers. Since the vertical arc fiberizing apparatus can be adjusted for a minimum delay time of 0.5 second, two methods of achieving shorter delay times were evaluated.

In the first method, called drip fiberizing, molten droplets were formed on a rod by the arc and were permitted to fall directly into the annular nozzle. The blast was started manually the instant a droplet left the rod and was stopped automatically by the blast duration timer. The blast pressure was varied from 250 to 450 psi. The annular nozzle was located at 6.5 and 16.5 inches below the arc to provide calculated delay times of 0.135 and 0.292 second. The results of these tests, conducted with R-76, are given in Table I.

TABLE I

DRIP FIBERIZING STUDIES WITH R-76

Blast Pressure PSI	Blast Duration Seconds	Distance of Nozzle Below Arc, Inches	Fiber Yield, Gms/50 Blasts	Comments
250	0.9	6.5	0.4	Very fine fibers
300	0.9	6.5	1.5	Very fine fibers
450	0.9	6.5	1.0	Very fine fibers
300	0.9	16.5	0.5	Very fine fibers

The highest yield with the drip fiberizing method was 1.5 grams per fifty blasts as compared with 3.6 grams with the previous method for R-76. The lower indicated fiber yield, however, should not be construed as conclusive evidence of the inefficiency of the drip fiberizing method for two reasons which prevent a valid comparison: (a) the amount of material in each droplet is somewhat less than the amount of material which can be removed

from the rod by a direct blast, and (b) the droplets fall continually from the rod which remains in the arc with no time-consuming intermittent cooling and reheating. It is therefore possible that perfection of the drip fiberizing method may result in a greater fiber yield per unit time than the intermittent method.

The second method of achieving shorter delay times consisted of reconstructing the 20 degree annular nozzle in the shape of a horseshoe so that the rod could be quickly swing out of the arc and directly into the nozzle with no vertical motion of the nozzle. With this method, delay times as short as 0.1 to 0.2 second could be consistently achieved. The fiber yield was low - from one to three grams per fifty blasts - but was comparable with the yield reported earlier on the unmodified 20 degree annular nozzle. The operating ease of the "horseshoe nozzle" method was judged highly satisfactory.

B. Ceramic Fiber Compositions

During this period, 35 new fiber compositions were evaluated. Some were modifications of earlier promising compositions and the rest were based on conclusions derived from the literature on various glass-forming systems. The raw materials were processed into rods and fired according to the standard procedure previously established (Quarterly Report No. 2, pp 7 and 8). The compositions and fiberizing results are given in Table II. The results of fusion temperature tests of those materials which produced sufficient fibers are given in Table III. Included in this Table are tests of earlier compositions and a number of materials supplied by other companies.

Modifications of R-6: R-81 through R-85

Small amounts of five oxides were added to R-6 (zircon) in attempts to reduce its surface tension, to slow its solidification rate, and to lower its viscosity to within the operating range of the vertical fiberizing apparatus. None of the compositions could be fiberized, although the addition of both alumina (R-81) and magnesia (R-83) greatly lowered the viscosity. Alumina was somewhat more effective than magnesia. All of these compositions would require shorter delay times for quantity fiberizing.

Modifications of R-11: R-86 and R-87

For these two compositions, lead and zinc oxides were added to R-11 (SiO_2 - 50; ZrO_2 - 50). The fiber yield was increased from the original 0.8 gm per fifty blasts by both oxides, zinc oxide being more effective. The fusion temperature of both compositions, 1680°C, was high enough to justify further studies.

First Modifications of R-21: R-88 through R-90

Composition R-21 (Al_2O_3 - 40; SiO_2 - 20; ZnO - 40) was modified by increasing each of the three respective constituents in an effort to increase its yield. The only composition showing an improvement was R-89, which contained increased silica. Its fusion temperature, 1810°C, was still very high. Both R-88 and R-90 were dropped from further consideration.

Modifications of R-58: R-91 through R-93

This series consisted of changing the molar ratio of magnesia to alumina (keeping the silica constant) as follows:

	Molar Ratio $MgO:Al_2O_3$
R-58 (original)	1.000:0.866
R-91	1.000:5.000
R-92	1.000:2.300
R-93	1.000:0.666

It is not understood why none of these three compositions did not have as high a fiber yield as R-58 (three grams per fifty blasts). With a two-gram yield and a fusion temperature of 1620°C, R-91 was the only material worthy of further study.

Barium Spinel: R-94 and R-95

Pure barium spinel, R-94, interestingly had a slightly better tendency to fiberize than pure magnesium spinel, R-5.

However, neither R-94 nor R-95 (with 23% silica) produced a yield high enough to warrant further studies.

Antimony Oxide Glasses: R-96 through R-98

Although the melting point of antimony oxide is only 652°C, These compositions were studied to ascertain the glassforming characteristics of this oxide, which has been widely used in glass compositions. The rods were sintered at 1000°C since 1400°C would have completely melted them. Fibers were easily formed with each composition including R-97 which contained no silica, thus substantiating statements in the literature that antimony oxide strongly promotes glass formation. The yields of these compositions were surprisingly low. No further work with these glasses is planned, but antimony oxide may be used in small quantities as a glass-former - flux in future compositions.

Modifications of R-74: R-99 through R-103

These compositions consisted of the following modifications of R-74 designed to increase its fusion temperature: R-99, increase alumina/magnesia ratio; R-100, addition of tin oxide; R-101, partial substitution of alumina with chromium oxide; R-102, partial substitution of alumina with samarium oxide; and R-103, addition of cerium oxide. The only composition in this series with a satisfactory fiber yield was R-99. Its yield was comparable to that of R-74 and the fusion temperature, 1580°C, was 120°C higher. The melting behavior of R-100 in the arc was peculiar and the droplets were difficult to manage. In spite of this, enough fibers were produced to perform a fusion temperature test. The chromium oxide in R-101 caused extremely rapid nucleation and no fibers could be formed. Both R-102 and R-103 completely melted during the 1400°C sintering which indicated the powerful fluxing action of samarium and cerium oxides. Studies with R-99 will continue.

High Melting Phosphate Glasses: R-104 through R-106

Compositions R-104 and R-106 were eliminated because of low fiber yield and melting during sintering, respectively.

Although the fiber yield of R-105 was low, its fusion temperature was determined. Further work is contemplated with other high melting phosphates because of their good glass-forming characteristics and widespread usage in special glasses.

Second Modification of R-21: R-107 through R-115

These compositions consisted of adding various fluxes (esp. glassformers) to the original R-21 in attempts to increase its fiber yield. Additions of vanadium oxide (R-107) and phosphorus pentoxide (R-109) lowered the melting point below 1400°C, resulting in their elimination. Improvements in fiber yield over R-21 were achieved with additions of antimony oxide (R-108), samarium oxide (R-110), and cerium oxide (R-112). Both R-108 and R-110 have fusion temperatures exceeding 1800°C. (The fusion temperature of R-112 has not yet been determined.) These three materials are very promising. The low fiber yields of R-111, R-114, and R-115 resulted in their elimination. The R-113 rods cracked on sintering and were not evaluated.

From the foregoing studies, eight new compositions were found to have the fiber yields and fusion temperatures required to warrant further studies.

TABLE II

NEW CERAMIC FIBER COMPOSITIONS

Composition Number	Material	Weight %	Optimum Blast Delay Time, Seconds	Fiber Yield, Gms/50 Blasts	Comments
R-81	ZrO_2	60.2		0	Glassy pellets
	Al_2O_3	10.0			
	SiO_2	29.8			
R-82	ZrO_2	56.0		0	
	BaO	16.3			
	SiO_2	27.7			
R-83	ZrO_2	60.2		0	Glassy pellets
	MgO	10.0			
	SiO_2	29.8			
R-84	ZrO_2	53.6		0	
	ZnO	20.0			
	SiO_2	26.4			
R-85	ZrO_2	53.6		0	
	TiO_2	20.0			
	SiO_2	26.4			
R-86	ZrO_2	45.0	0.5	1.2	Droplets very viscous
	SiO_2	45.0			
	PbO	10.0			
R-87	ZrO_2	40.0	0.5	2.0	Droplets very viscous
	SiO_2	40.0			
	ZnO	20.0			

R-88	SiO_2	20.0	1.0	0.3	Rods thermal shocked severely, very fine fibers
	Al_2O_3	60.0			
	ZnO	20.0			
R-89	SiO_2	35.0	1.0	1.5	Medium sized, good quality fibers
	Al_2O_3	32.5			
	ZnO	32.5			
R-90	SiO_2	20.0	1.0 - 2.0	Trace	Extremely fine fibers
	Al_2O_3	20.0			
	ZnO	60.0			
R-91	SiO_2	25.0	3.5	2.0	Fine fibers, 2 - 4 inches long
	Al_2O_3	62.5			
	MgO	12.5			
R-92	SiO_2	25.0	2.0	0.6	Fine fibers
	Al_2O_3	52.5			
	MgO	22.5			
R-93	SiO_2	25.0		0	
	Al_2O_3	30.0			
	MgO	45.0			
R-94	BaO	21.6	3	0.1	Several glassy fibers
	Al_2O_3	78.4			
R-95	BaO	12.5	2	0.6	Very fine fibers
	Al_2O_3	64.5			
	SiO_2	23.0			
R-96	Sb_2O_3	65.0	1.0	0.2	1000°C sinter, fine glassy fibers
	Al_2O_3	12.8			
	Na_2O	0.3			
	K_2O	0.1			
	SiO_2	21.8			

R-97	Sb_2O_3	72.0	1.0	0.1	1000°C sinter, few glassy fibers, 1/8 - 1/2 inch long
	Al_2O_3	16.8			
	MgO	11.2			
R-98	Sb_2O_3	57.6	1.0	0.3	1000°C sinter, very fine glassy fibers
	Al_2O_3	11.5			
	SiO_2	23.2			
	MgO	7.7			
R-99	SiO_2	50.0	1.0	6.6	Long flexible fine fibers
	ZrO_2	20.0			
	Al_2O_3	27.0			
	MgO	3.0			
R-100	SiO_2	43.5	2.0	1.0	Medium sized, 1 - 6 inches long
	ZrO_2	17.5			
	Al_2O_3	19.5			
	MgO	6.5			
	SnO_2	13.0			
R-101	SiO_2	50.0		0	Dark green glassy pellets but no fibers
	ZrO_2	20.0			
	Al_2O_3	7.5			
	MgO	7.5			
	Cr_2O_3	15.0			
R-102	SiO_2	50.0			Melted in 1400°C sinter
	ZrO_2	20.0			
	Al_2O_3	15.8			
	MgO	7.5			
	Sa_2O_3	6.7			

R-103	SiO_2	43.5			Melted in 1400°C sinter
	ZrO_2	17.5			
	Al_2O_3	19.5			
	MgO	6.5			
	CeO_2	13.0			
R-104	SrO	60.0		0	A few glassy tails and pellets
	P_2O_5	40.0			
R-105	SrO	55.0	1.0 - 2.0	1.6	Very fine fibers, 1 - 2 inches long
	P_2O_5	25.0			
	SiO_2	20.0			
R-106	CaO	44.8			Melted in 1400°C sinter
	P_2O_5	40.4			
	SiO_2	14.8			
R-107	SiO_2	17.9			Melted in 1400°C sinter
	Al_2O_3	35.7			
	ZnO	35.7			
	V_2O_5	10.7			
R-108	SiO_2	17.9	1.0	1.3	Very fine fibers, 1 - 2 inches long
	Al_2O_3	35.7			
	ZnO	35.7			
	Sb_2O_3	10.7			
R-109	SiO_2	16.7			Melted in 1400°C sinter
	Al_2O_3	33.3			
	ZnO	33.3			
	P_2O_5	16.7			
R-110	SiO_2	18.5	2.0	1.2	Very fine fibers, 1/2 - 2 inches long
	Al_2O_3	37.0			
	ZnO	37.0			
	Sa_2O_3	7.5			

R-111	SiO_2	18.5	2.0	0.1	Very fine short fibers
	Al_2O_3	37.0			
	ZnO	37.0			
	Fe_2O_3	7.5			
R-112	SiO_2	17.9	1.0	1.4	Fine fibers 1/2 - 1 inch long
	Al_2O_3	35.7			
	ZnO	35.7			
	CeO_2	10.7			
R-113	SiO_2	18.5			Rods cracked in sintering; not evaluated
	Al_2O_3	37.0			
	ZnO	37.0			
	Y_2O_3	7.5			
R-114	SiO_2	19.8	1.0	0.6	Very fine fibers, many glassy pellets
	Al_2O_3	37.0			
	ZnO	37.0			
	PbO	4.7			
	B_2O_3	1.5			
R-115	SiO_2	18.5	1.0	0.4	Very fine fibers, many glassy pellets
	Al_2O_3	37.0			
	ZnO	37.0			
	SnO_2	7.5			

TABLE III

FUSION TEMPERATURES OF SELECTED COMPOSITIONS AND COMMERCIAL MATERIALS

Material	Fusion Temperature °C
E-Glass	950
CMP Paper[a]	1100
CMG Paper[a]	1225
CM Paper[a]	1325
R-105	1350
R-100	1420
R-59	1450
R-74	1450
R-45	1475
R-58	1495
R-79	1550
R-99	1580
R-76	1605
R-91	1620
Fiberquartz FQ-RCl[b]	1625
Refrasil AA	1625
R-86	1680
R-87	1680
R-11	1700
Fiberfrax (fine)[d]	1740
Cerafelt[e]	1770
Fiberfrax (medium)[d]	1780
R-89	1810

Zircon[c]	1815
Zirconia A[c]	>1830 (considerable bloating)
Zirconia B[c]	>1830
R-21	>1830
R-108	>1830
R-110	>1830

a. Minnesota Mining and Manufacturing, St. Paul, Minn.

b. Seaman Products, Sylmar, Calif.

c. H. I. Thompson Fiber Glass Company, Los Angeles, Calif.

d. Carborundum Company, Niagara Falls, N. Y.

e. Johns-Manville, New York, N. Y.

C. Continuous Fiberizing

A 10 KVA Lepel induction heating power supply was recently made available for this program. This unit is now being installed and will be set up for studying continuous production fiberizing of several selected high yield compositions. The anticipated method for initial studies consists of melting a material in a refractory crucible and allowing it to flow out through an orifice in the bottom of the crucible into an annular ring fiberizing nozzle.

Recent reports on studies of crucibles for containing high melting glasses has indicated that niobium diboride undergoes no reaction with silica up to 2200°C. Several other borides and nitrides were successfully used above 2000°C.

D. Fiber-Resin Composites

A brief study was conducted on a method of felting bulk blown fibers. About ten grams of R-74 fibers were agitated rapidly in water with a Waring Blendor. The fibers were well dispersed and the pellets were broken off by the agitation; however, the fibers were reduced to 1/4 to 3/4 inch lengths. Following a short settling period to remove the pellets, the fibers in suspension were poured into a Buchner funnel connected to a vacuum aspirator. The resulting felt was free of pellets, very uniform in texture and thickness, and the fibers were randomly oriented and well intermeshed in the plane of the felt. The felt was quite strong enough to be handled and shaped over intricate contours and its open structure was judged highly amenable for resin impregnation. The process is easily adaptable to utilize an anhydrous suspension fluid to minimize reduction of fiber strength by the presence of water.

IV. PROGRAM FOR NEXT INTERVAL

1. Complete studies of the following compositions:

   a. Modifications of R-76 to increase fiber yield (R-116 — R-125)

   b. Aluminum phosphate glasses (R-126 — R-133)

   c. Calcium aluminate glasses (R-134 — R-139)

   d. Calcium silico-fluoride glasses (R-140 — R-143)

   e. Additional modifications of selected compositions (R-144 — R-150)

2. Conduct further studies of fiber felting and impregnating techniques.

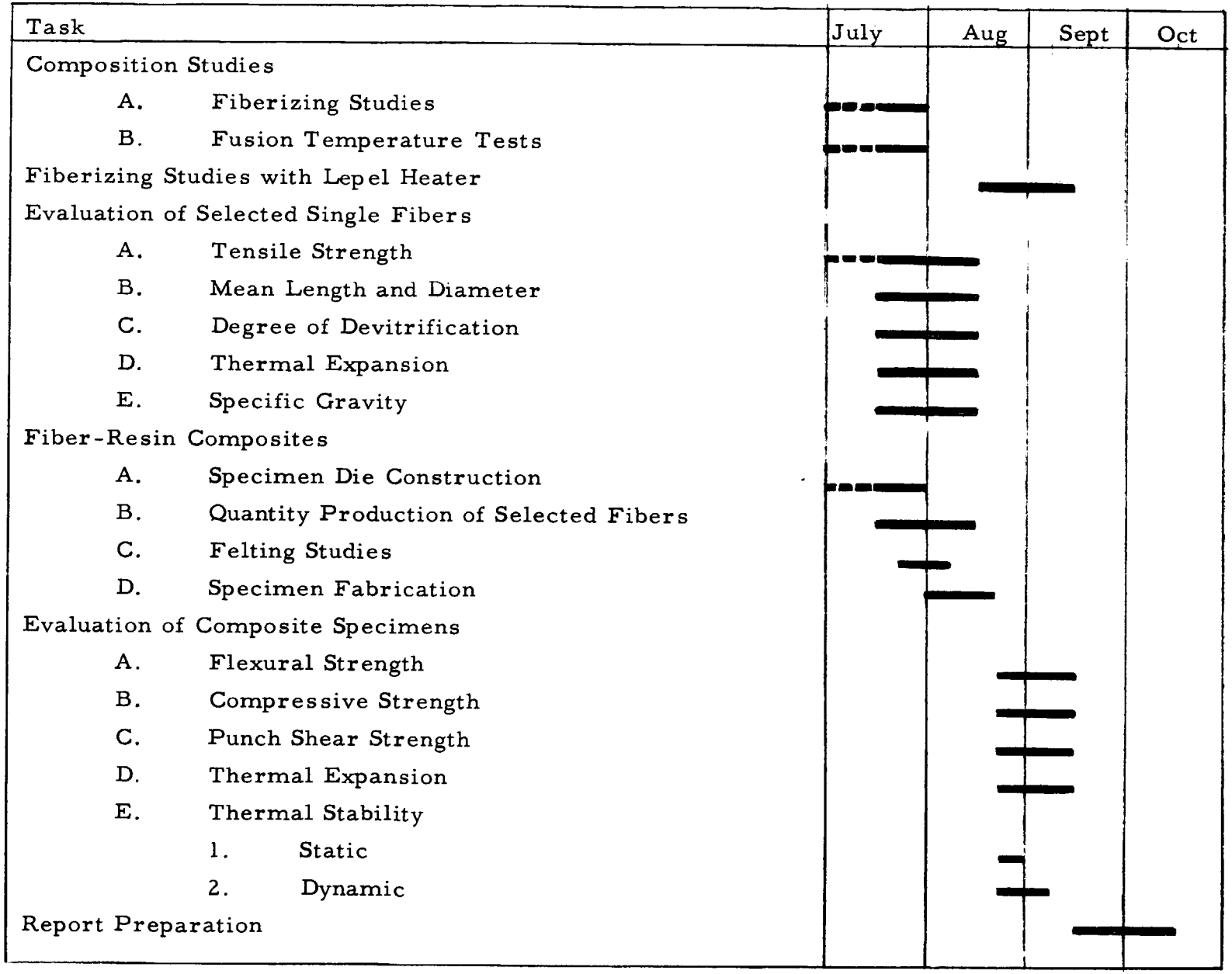
3. Produce sufficient quantities of fibers from the most promising compositions for fabrication of fiber-resin composite specimens.

4. Conduct property tests on composite specimens and single fibers as outlined.

5. Perform studies of continuous fiberizing methods with Lepel Induction Heater.

The tentative work schedule for the final period is shown on Page 18.

TENTATIVE WORK SCHEDULE FOR FINAL PERIOD



V. PERSONNEL

The personnel of the Ceramics Development Group assigned to this project are listed below:

L. E. Gates	Member of Technical Staff	Project Head
W. E. Lent	Associate Engineer	Fiber Production
W. T. Teague	Member of Technical Staff	Continuous Fiberizing and Composite Testing

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